molecules

MDPI

Supporting info

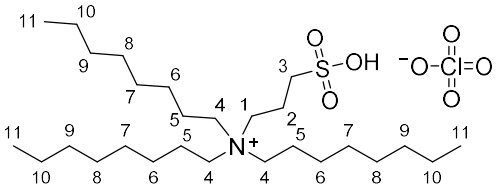
Electrophilic Bromination in Flow: a Safe and Sustainable Alternative to the Use of Molecular Bromine in Batch: Supporting Info

Reinout Van Kerrebroeck [1], Pieter Naert [1], Thomas S.A. Heugebaert [1], Matthias D'hooghe [1] and Christian V. Stevens [1,*]

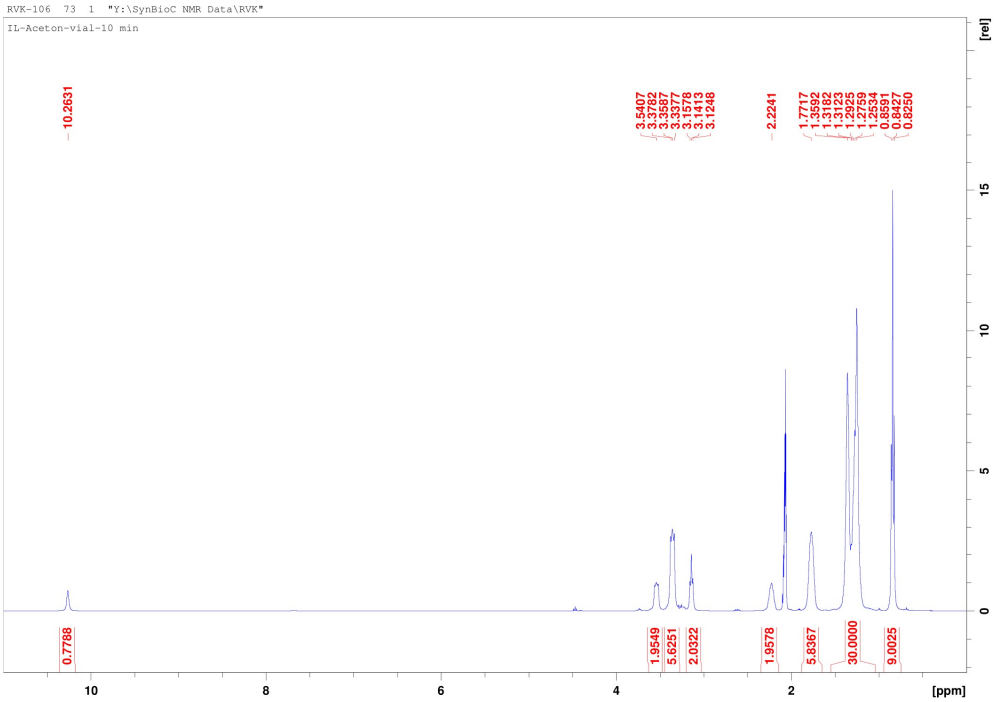
[1] SynBioC research Group, Department of Green Chemistry and Technology, Ghent University, Coupure Links 653, 9000 Ghent, Belgium

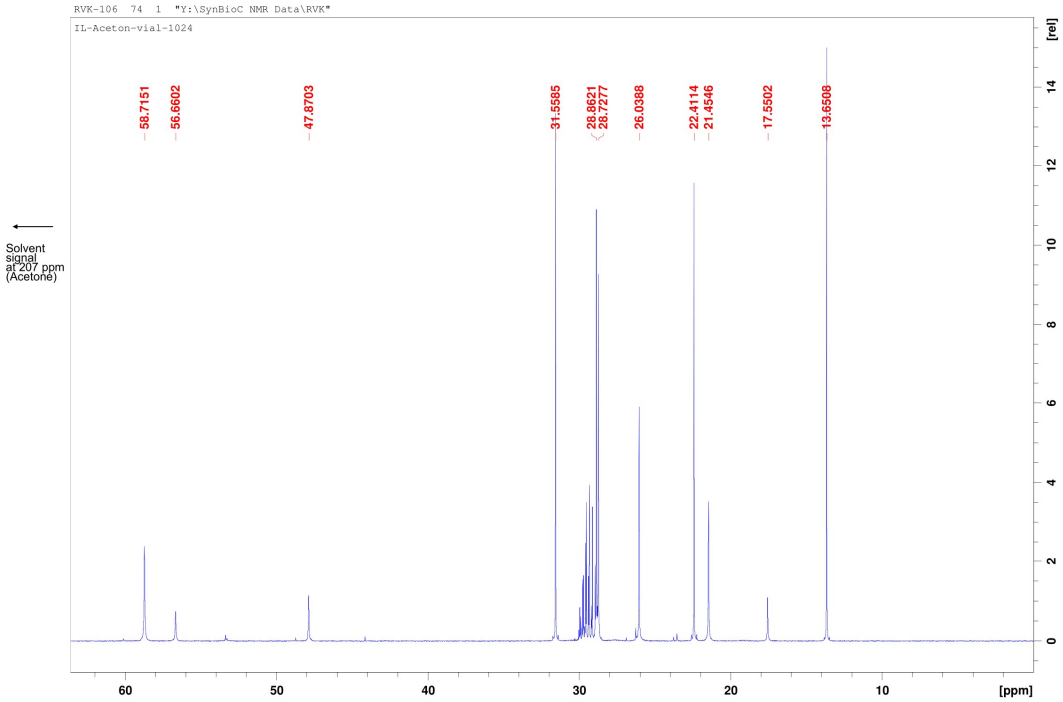
* Correspondence: Chris.Stevens@UGent.be

1. Trioctyl-(3-sulfopropyl)ammonium perchlorate 4



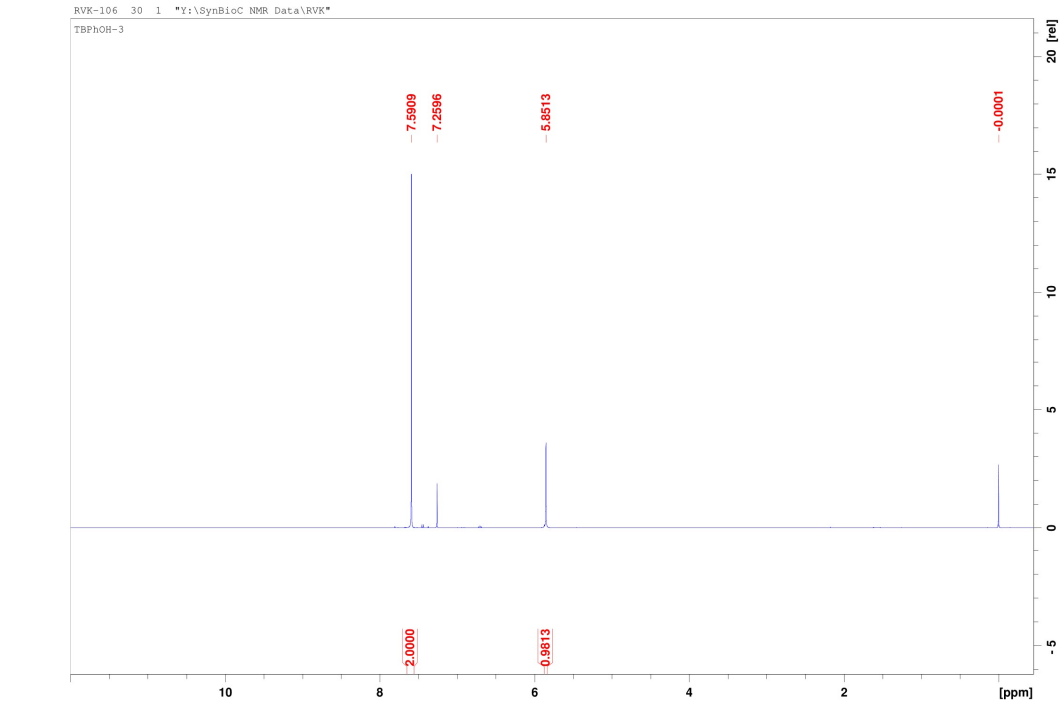
^{1}H NMR (400 MHz, acetone-d_6): δ=0.84 (t, J=7Hz, 9H; $C^{11}\underline{H}_3$), 1.25-1.35 (m, 30H; $C^{6\text{-}10}\underline{H}_2$), 1.77 (br. s, 6H, $C^5\underline{H}_2$), 2.22 (br. s, 2H, $C^2\underline{H}_2$), 3.14 (t, J=7Hz, 2H; $C^3\underline{H}_2$, 3.58 (br. t, J=8Hz, 6H; $C^4\underline{H}_2$), 3.35 (m, 2H; $C^1\underline{H}_2$), 10.26 (br. s, D_2O-exch. $SO_3\underline{H}$); ^{13}C NMR (100 MHz, acetone-d_6), 13.7 ($\underline{C}^{11}$), 17.6 ($\underline{C}^2$), 21.5 ($\underline{C}^5$), 22.4 ($\underline{C}^{10}$), 26.0 ($\underline{C}^6$), 28.7 ($\underline{C}^7$), 28.9 ($\underline{C}^8$), 31.6 ($\underline{C}^9$), 47.9 ($\underline{C}^3$), 56.7 ($\underline{C}^1$), 58.7 ($\underline{C}^4$).

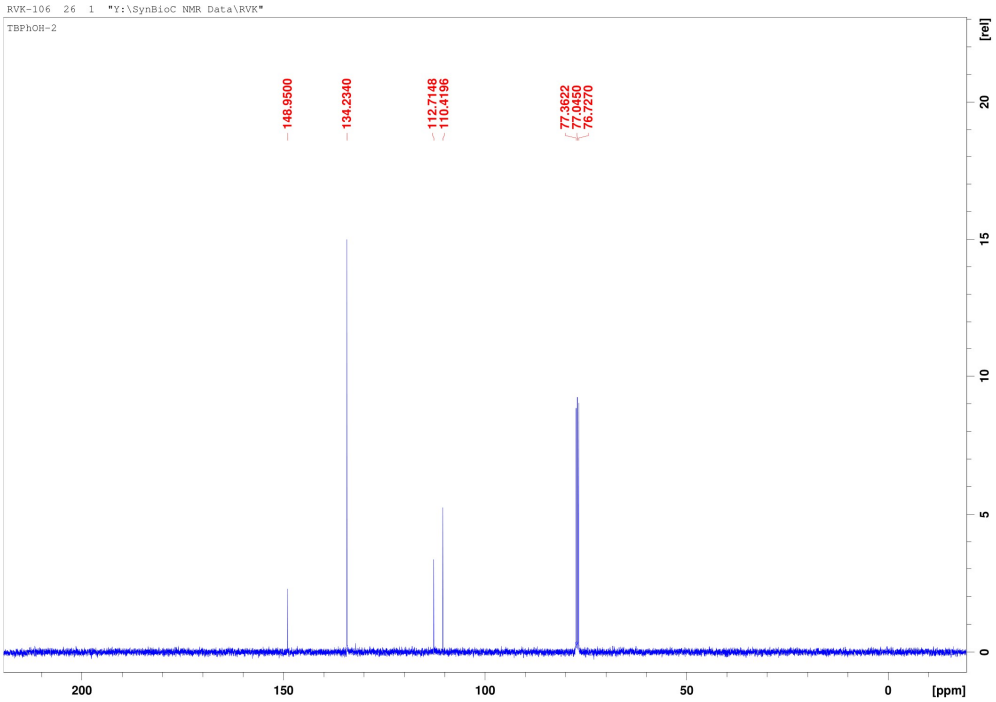




2. 2,4,6-Tribromophenol

2,4,6-Tribromophenol: ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.85 (s, 1H, O<u>H</u>), 7.59 (s, 2H, $C^{3,5}$<u>H</u>); ^{13}C NMR (100 MHz, $CDCl_3$): δ=110(<u>C</u>^{2,6}Br), 112 (<u>C</u>^{4}Br), 134 ($C^{3,5}$H), 149 (C^{1}OH). This is in accordance with the online available spectra [1].




RVK-106 26 1 "Y:\SynBioC NMR Data\RVK"
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134.2340
112.7148
110.4196
77.3622
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76.7270
[rel]
20
15
10
5
0
200
150
100
50
0
[ppm]

26

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    Last changed     : 12/01/2015 9:22:18 by JB
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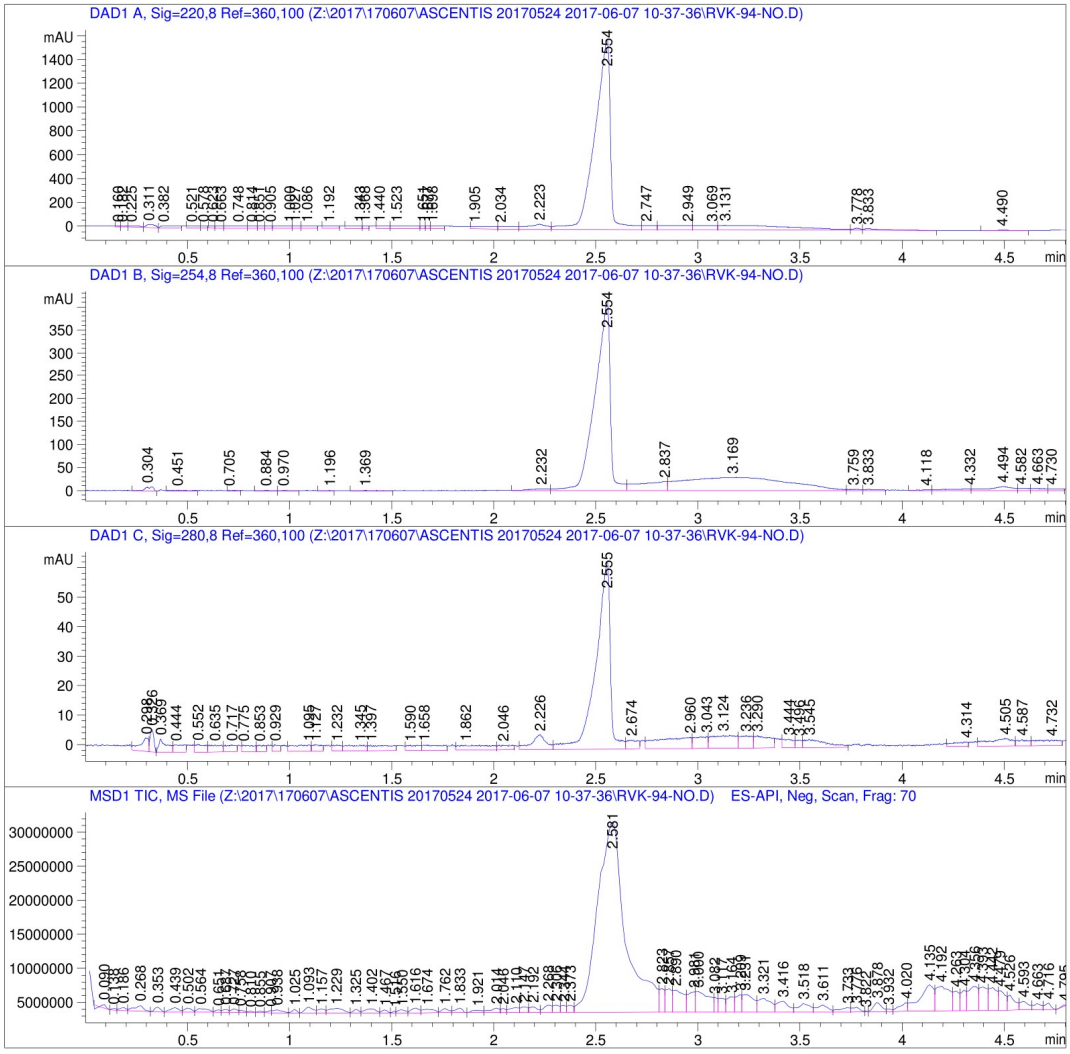
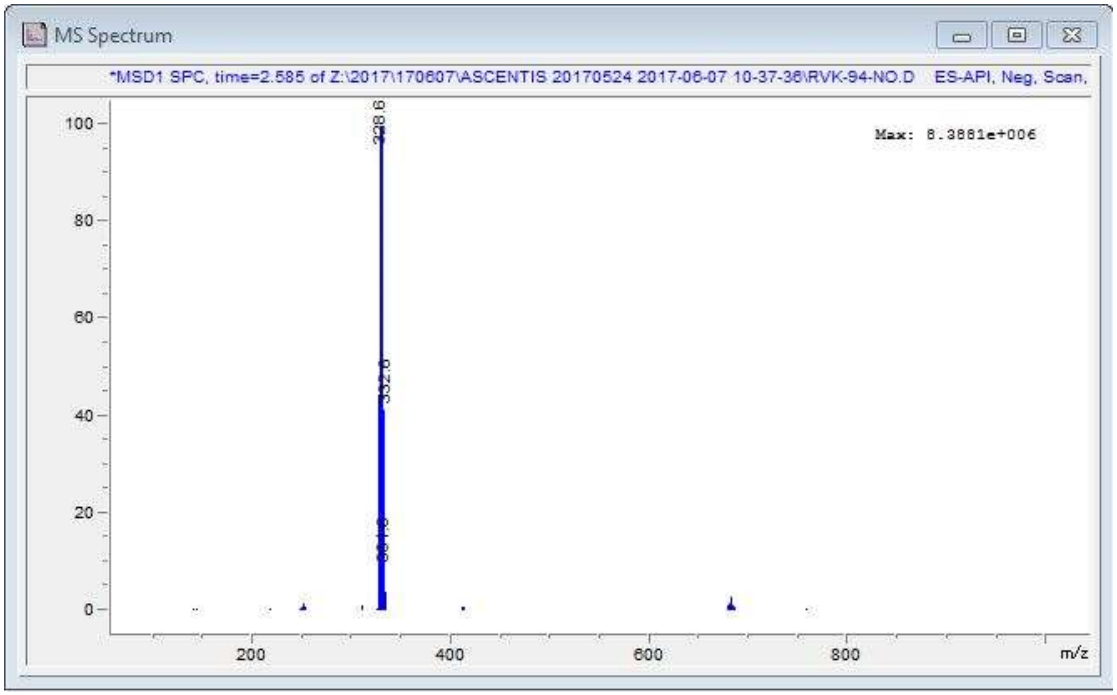
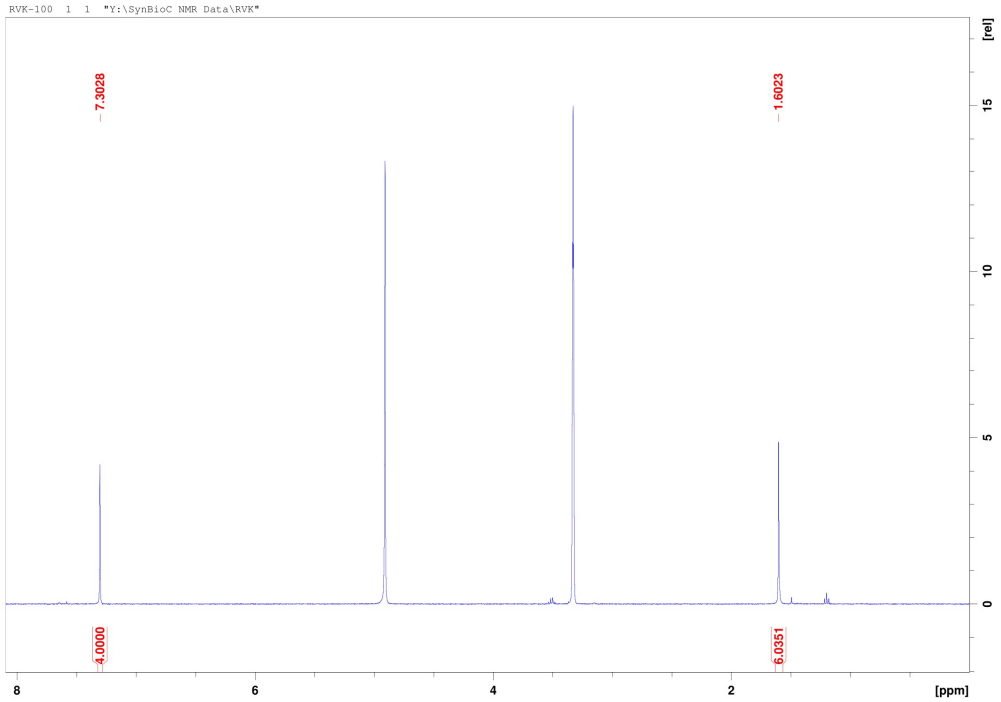




28

29 **3. 2,2′,6,6′-Tetrabromobisphenol A**

30 2,2′,6,6′-Tetrabromobisphenol A: ^{1}H NMR (400 MHz, MeOD-d_4): δ=1.61 (s, 6H; C$\underline{H}_3$), 4.91 (s,
31 D_2O-exch., O$\underline{H}$), 7.30 (s, 4H, C$\underline{H}$); ^{13}C NMR (100 MHz, MeOD-d_4): δ=30 ($\underline{C}H_3)_2$, 41 ($\underline{C}_{quat}$), 111 ($\underline{C}$Br)$_4$,
32 130 ($\underline{C}$H)$_4$, 144 ($\underline{C}$C)$_2$, 149 ($\underline{C}$O)$_2$ This is in accordance with the online available spectra [2].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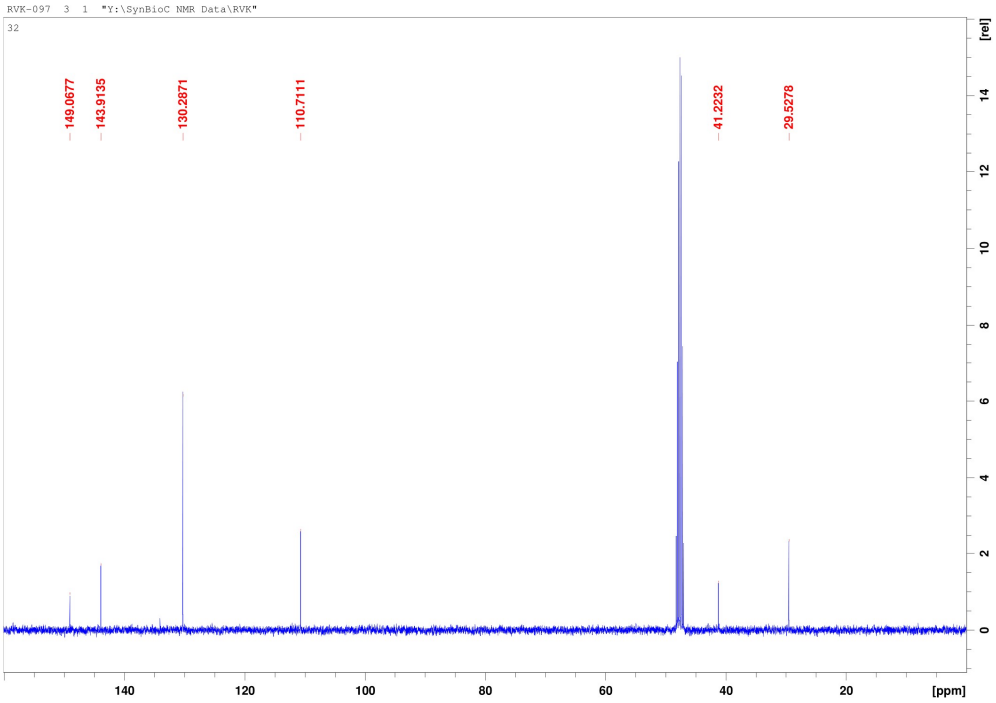
4.0000
6.0351
[rel]
[ppm]

33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[ppm]

34

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    Last changed     : 12/01/2015 9:22:18 by JB
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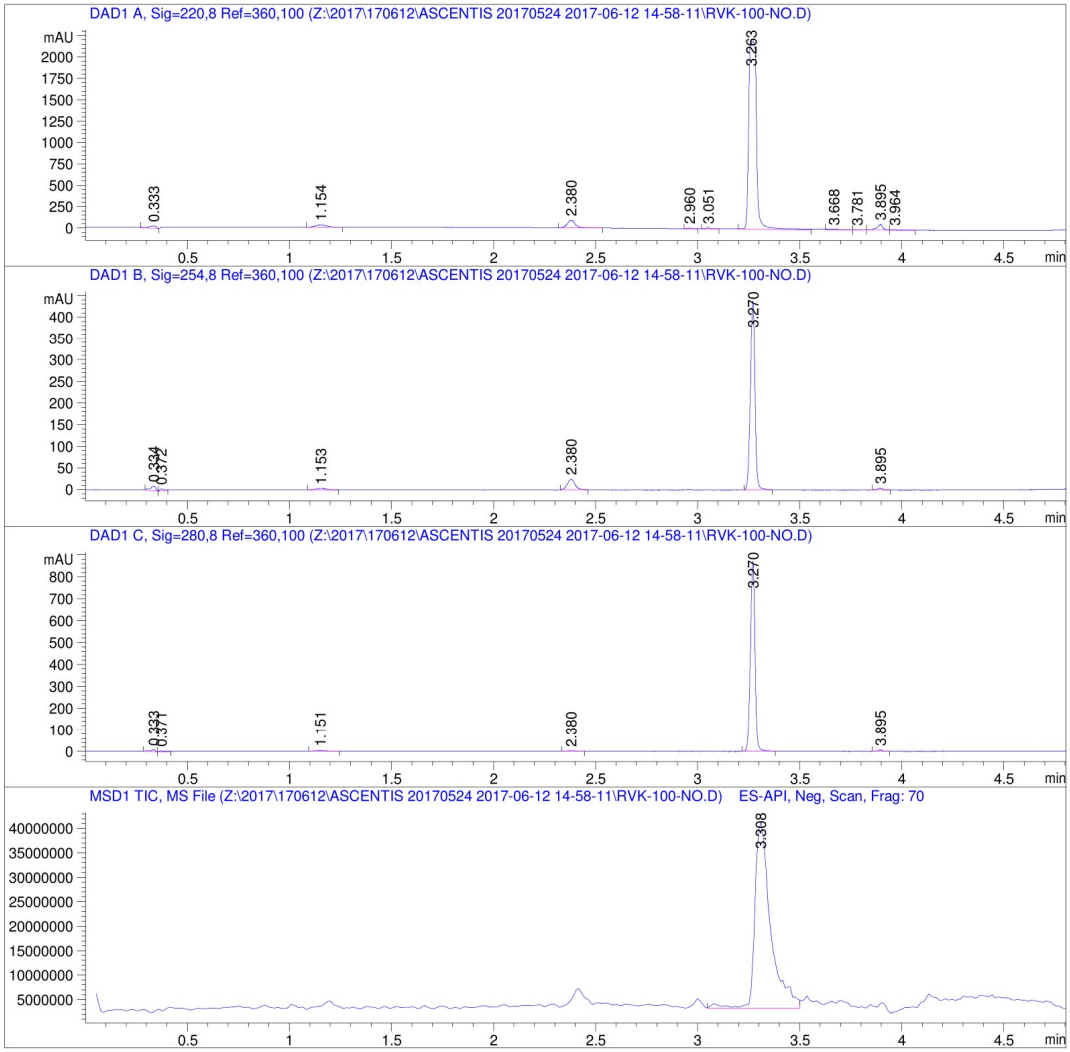

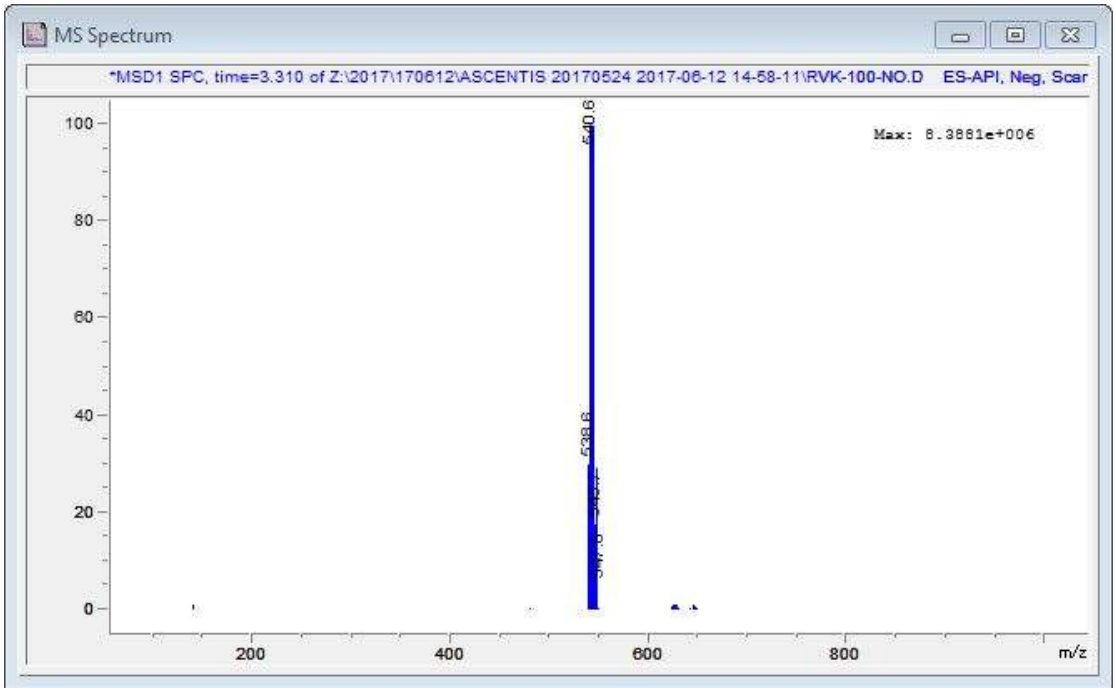

36

37 **4. 1,2,5,6,9,10-Hexabromocyclododecane**

38 Due to the multitude of chiral positions this product could not be analysed with NMR. Since the
39 industrial application of hexabromocyclododecane, being an additive flame retardant, relies solely
40 on the amount of bromine present and not on the enantiomeric or diastereomeric structure, checking
41 the mass on LC-MS to detect possible underbromination, producing the unsaturated tetrabrominated
42 product, or overbromination, producing the hepta- or octabrominated product was deemed
43 sufficient. It can be seen on the LC-MS that there are multiple diastereomers, but no products with a
44 different mass.

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Data File Z:\2018\180702\ASCENTIS 20180417 2018-07-02 13-32-24\RVK-215-1MIN.D
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                                               Inj Volume : 2.0 µl
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Last changed    : 12/01/2015 9:22:18 by JB
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Last changed    : 30/03/2019 15:27:36 by SD
Method Info     : Ascentis column method for Synthesis samples
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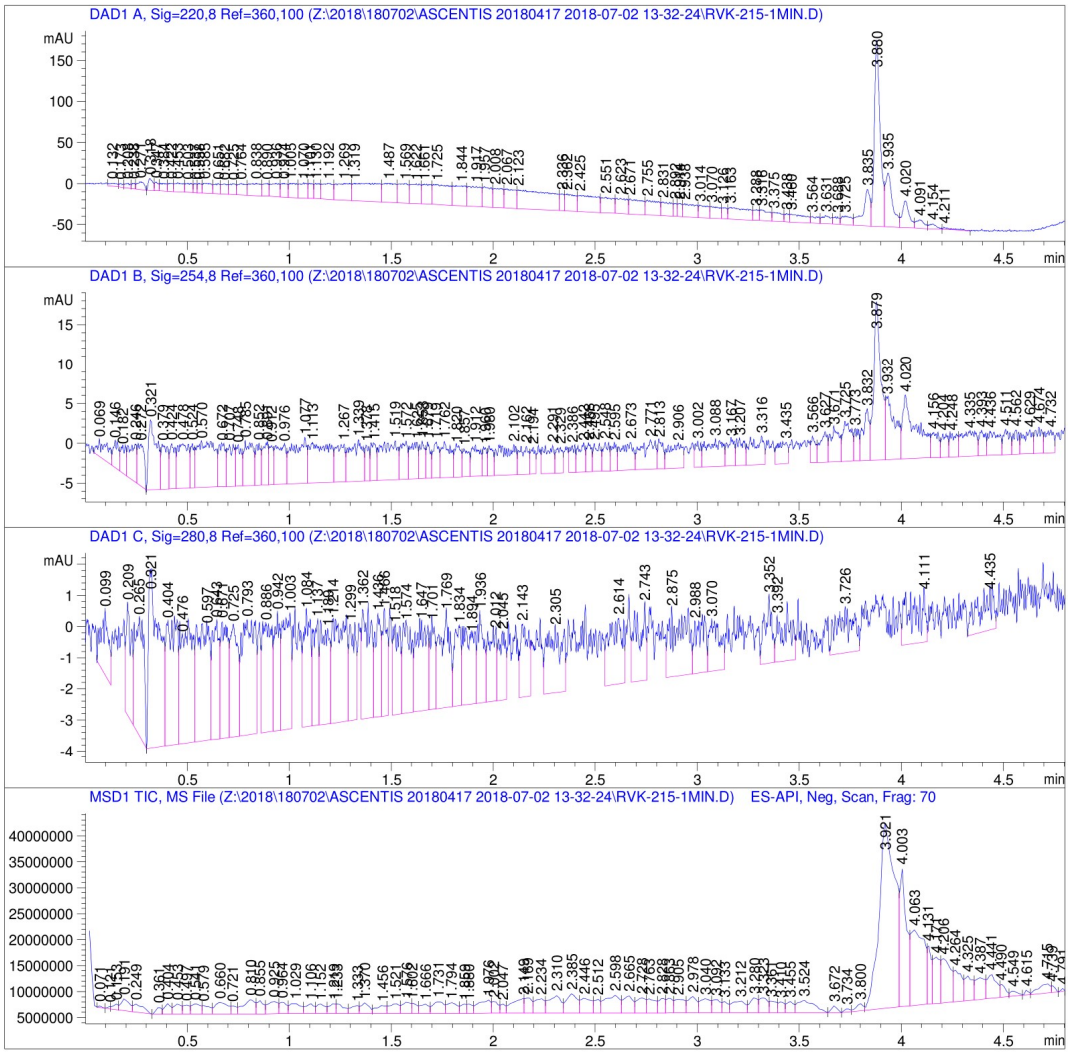


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Instrument 1 24/05/2019 9:50:58                    Page   1 of 7
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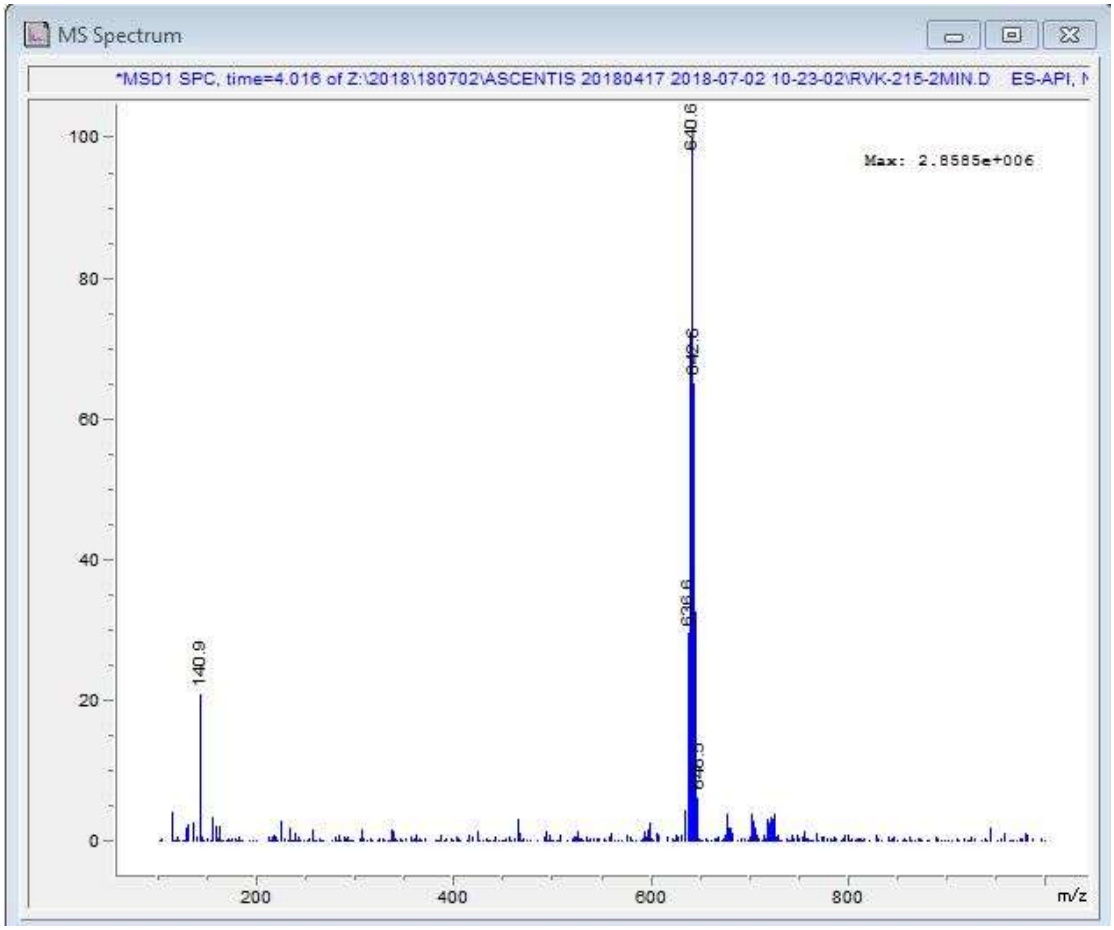
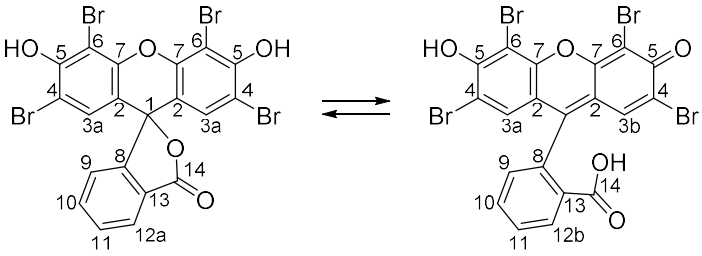
The MS-spectrum at 3.921 minutes is given below:

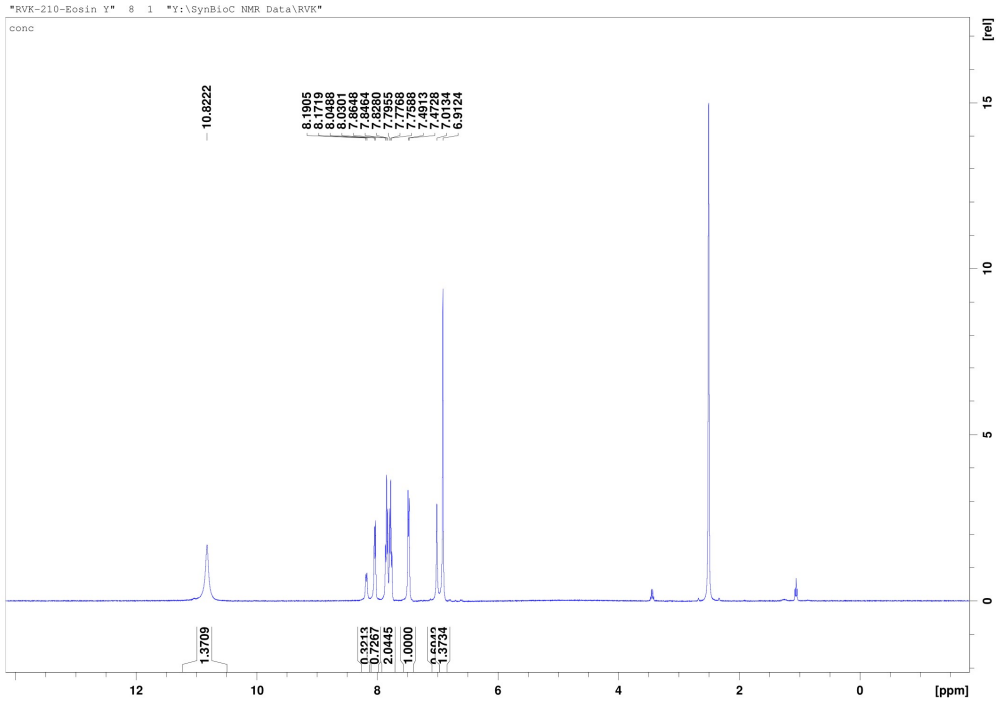


5. Eosin Y



The ^{1}H-NMR spectrum of eosin Y is difficult to interpret, because it appears as two tautomeric forms. The difference between these two can be seen in the 3 position, and the partial disappearance of the C^{5}OH-proton, and a slight shift of the 12a-b position The ratio between the two tautomers is approximately 7/3. This ratio is not fixed, and the equilibrium can be shifted by addition of D_2O. The effects of this tautomerism are too small to notice in the ^{13}C-NMR spectrum.

Eosin Y: ^{1}H NMR (400 MHz, DMSO-d$_6$): δ=6.91 (s, 1.4H, C^{3a}H), 7.11 (s, 0.6H, C^{3b}H), 7.48 (d, J=7Hz, 1H, C^{9}H), 7.77 (t, J=7Hz, 1H, C^{11}H), 7.84 (t, J=7Hz, 1H, C^{10}H), 8.03 (d, J=7Hz, 0.7H, C^{12a}H), 8.18 (d, J=7Hz, 0.3H, C^{12b}H), 10.82 (br. s, 1.6H, C^{5}OH); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ=81 (C^{1}), 101 (C^{4}), 108 (C^{6}), 113 (C^{2}); 124.7 (C^{9}), 125.7 (C^{12}), 126.2 (C^{11}), 130 (C^{3}), 131 (C^{13}), 137 (C^{10}), 148 (C^{5}), 151 (C^{8}), 154 (C^{7}), 168 (C^{14}). This is in accordance with the online available spectra [4].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8.1905
8.1719
8.0488
8.0301
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7.8280
7.7955
7.7768
7.7588
7.4913
7.4728
7.0134
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1.0000
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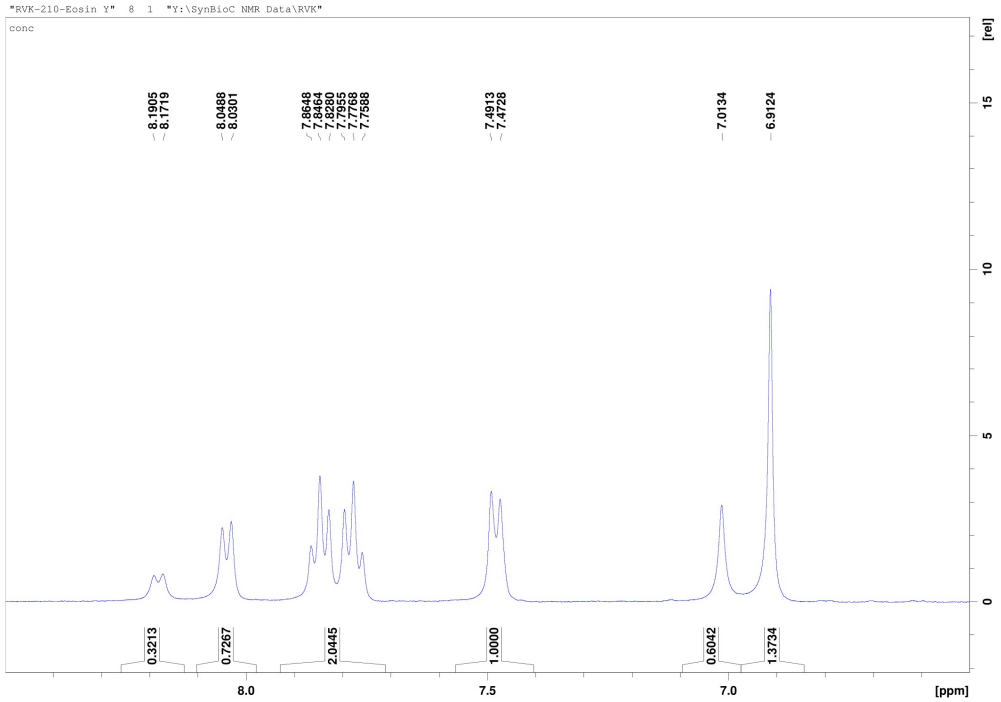
1.3734
[rel]
[ppm]

69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conc
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8.1719
8.0488
8.0301
7.8648
7.8464
7.8280
7.7955
7.7768
7.7588
7.4913
7.4728
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2.0445
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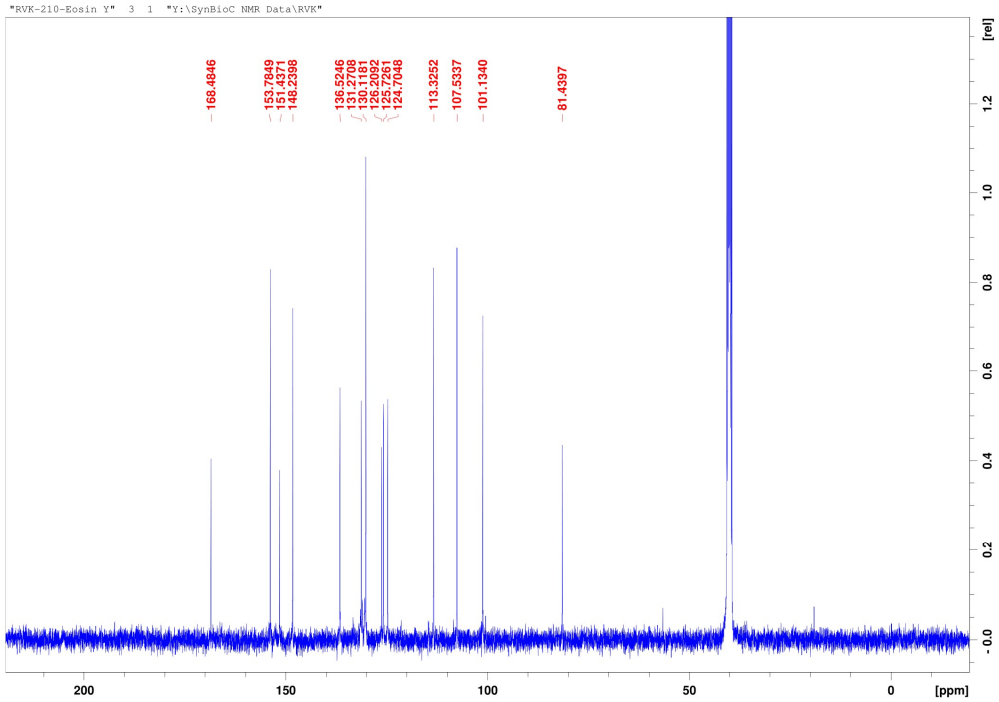
1.3734
[rel]
[ppm]

70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151.4371
148.2398
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130.1151
129.3982
125.7261
124.7048
113.3252
107.5337
101.1340
81.4397
[rel]
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0.4
0.2
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200
150
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[ppm]

71

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                                                  Inj Volume : 2.0 µl
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Last changed    : 28/12/2016 19:44:32 by YM
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Last changed    : 28/05/2019 14:53:15
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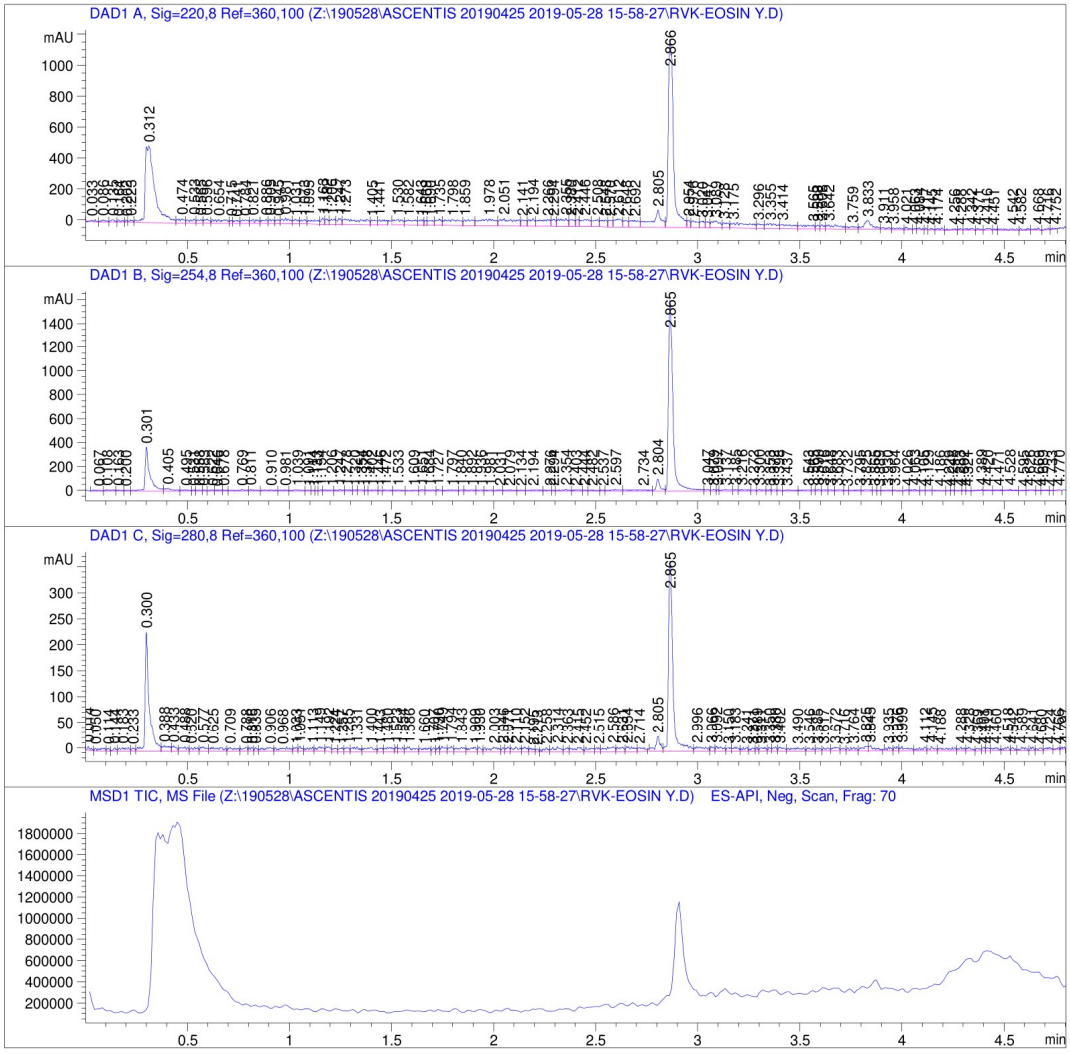

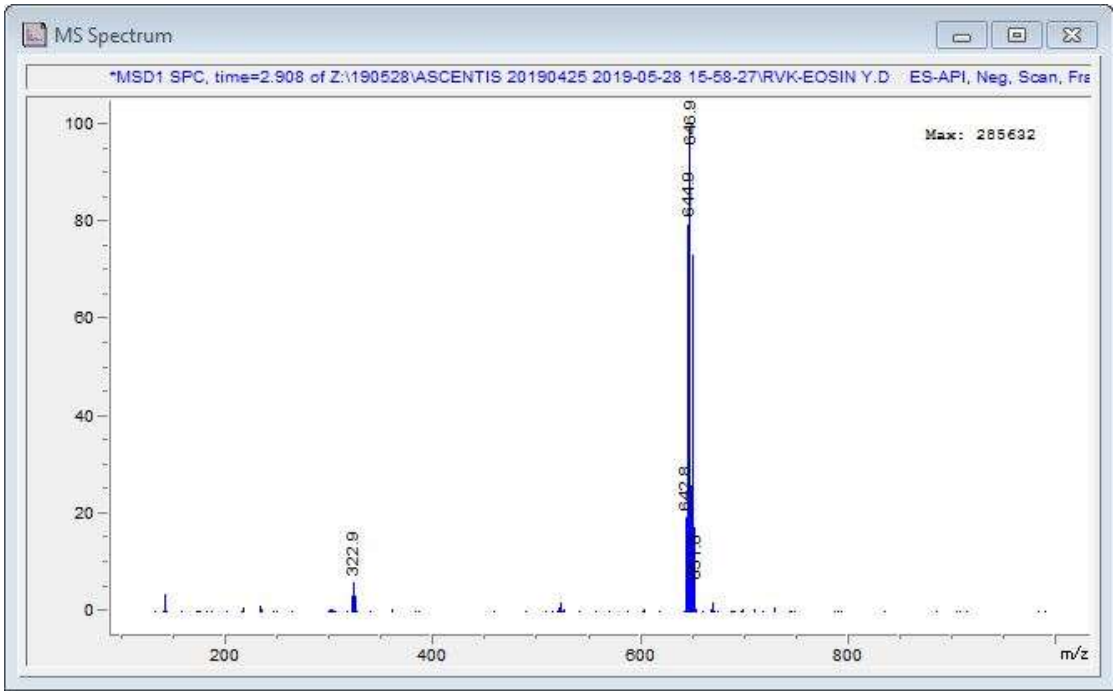

References

1. Sigma Aldrich spectral database 2,4,6-Tribromophenol. *Merck* https://www.sigmaaldrich.com/spectra/fnmr/FNMR001079.PDF
2. Sigma Aldrich spectral database 2,2',6,6'-Tetrabromobisphenol A *Merck* https://www.sigmaaldrich.com/spectra/fnmr/FNMR006985.PDF
3. SDBS Bromothymol Blue. *National Institute of Advanced Industrial Science and Technology (AIST)* https://sdbs.db.aist.go.jp/sdbs/cgi-bin/landingpage?sdbsno=1762
4. SDBS 2',4',5',7'-Tetrabromofluorescein. *National Institute of Advanced Industrial Science and Technology (AIST)* https://sdbs.db.aist.go.jp/sdbs/cgi-bin/landingpage?sdbsno=7510